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(54) POLYPHENYLENE ETHER RESIN COMPOSITION

(57) Abstract:

PURPOSE: To provide a polyphenylene ether resin compsn. which is excellent in the balance among fluidity, heat resistance, and impact resistance and suitable for a large molding.

CONSTITUTION: The compsn. comprises 15-50 pts.wt. polyphenylene ether resin, 15-60 pts.wt. arom. alkenyl compd. polymer, 10-20 pts.wt. resin component

comprising at least one hydrogenated A-B-A block copolymer (wherein A is an arom. alkenyl compd. polymer block; and B is a diene hydrocarbon polymer block) having a content of polymer block A higher than 50wt.% and at least one hydrogenated A-B-A block copolymer (wherein A and B are each the same as above-mentioned) having a content of polymer block A of 50wt.% or lower, and 1-20 pts.wt. arom. vinyl-grafted ethylene (co)polymer having a high graft efficiency.

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## Notes:

1. Untranslatable words are replaced with asterisks (\*\*\*\*).
2. Texts in the figures are not translated and shown as it is.

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## FULL CONTENTS

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### [Claim(s)]

[Claim 1] (A) The polymer 15 of polyphenylene ether resin 15 - 50 weight sections, and (B) alkenyl aromatic compound - 60 weight sections, (C) (C-1) A-B-A mold block copolymer ([ A / A and ]) [ of an alkenyl aromatic compound ] [ polymerization-] As for B, the resin with which it is a polymerization block or its hydrogenation object of a diene system hydrocarbon compound, and the content of A exceeds 50 weight % is a kind and an A-B-A (C-2) mold block copolymer ([ A / A and ]) at least. [ of an alkenyl aromatic compound ] [ polymerization-] B is a polymerization block or its hydrogenation object of a diene system hydrocarbon compound, and the content of A in total the combination at least with a kind of 50 or less weight % of resin 10 - 20 weight section, (D) The resin composition object which consists of the ethylene system (\*\*) polymer-aromatic vinyl graft polymer 1 - 20 weight sections with high graft efficiency.

[Claim 2] An ethylene system (\*\*) polymer-aromatic vinyl graft polymer to polyolefine (D) A kind of radical copolymeric organic peroxide, or two or more sorts of mixture, The resin composition object according to claim 1 which is a polyolefine aromatic vinyl graft polymer with graft efficiency high under coexistence of an aromatic vinyl monomer and a radical polymerization initiator obtained by kneading with the polymer of a vinyl aromatic series monomer.

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### [Detailed Description of the Invention]

#### [0001]

[Industrial Application] This invention relates to the good polyphenylene ether system resin composition object of physical-properties balance heat-resistant [ for large-sized mold goods, such as an inner package panel of an automobile, / fluid / suitable / and heat-resistant / suitable ], and shock-proof (especially low-temperature impact resistance).

#### [0002]

[Description of the Prior Art] Polyphenylene ether resin is widely used in the industrial field from the thermal resistance being good. However, most activities by independent [ of this resin ] are not made with fluid lack. Generally the polymer alloy with polystyrene resin is used as denaturation PPE in order to compensate this fault. To raise shock resistance has been tried without this resin's running short of shock resistance practically, adding a variety of [ until now ] elastic bodies (elastomer), and spoiling an original property. As a typical thing of this elastomer, the A-B-A mold triblock copolymer or its hydrogenation object of the alkenyl aromatic compound A and conjugated diene compound B is raised. This elastomer of a series

of will not have resulted, by the time these addition realizes practical physical properties with sufficient balance, although the thing of various molecular weight is marketed. Although being the object with which this is compensated, adding polyolefin resin to the elastomer of the above-mentioned A-B-A mold, and raising a shock resistant is proposed in U.S. Pat. No. 4,166,055 and these 4,239,673 grades, compatibility runs short and is still inadequate.

[0003]

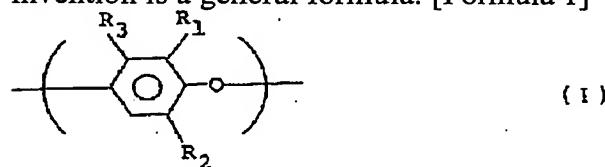
[Problem(s) to be Solved by the Invention] The technical problem of this invention is realizing the fluidity, thermal resistance, and shock resistance (cold shock) for which the ingredient suitable for large-sized mold goods, such as the trouble mentioned above, i.e., the inner package panel of an automobile etc., is asked with sufficient balance.

[0004]

[Means for Solving the Problem] In solving the above-mentioned technical problem, this invention persons added examination broadly about the addition effectiveness on the elastomer to add, the compatibility of a base polymer, and physical properties. [ two sorts of A-B-A mold triblock copolymers which, as a result, carry out specific range content of the A component or the hydrogenation object of those, and the high ethylene system (\*\*\*) polymer-aromatic vinyl graft polymer of the graft efficiency obtained by a process / \*\*\*\* / the after-mentioned ] By adding to polyphenylene ether system resin, it came to obtain the good ingredient of the suitable physical-properties balance for large-sized mold goods, and this invention was completed.

[0005] This invention Namely, (A) polyphenylene ether resin 15 - 50 weight sections, (B) The polymer 15 of an alkenyl aromatic compound - 60 weight sections, (C) (C-1) A-B-A mold block copolymer ([ A / A and ]) [ of an alkenyl aromatic compound ] [ polymerization-] As for B, the resin with which it is the hydrogenation object of a polymerization block of a diene system hydrocarbon compound, and the content of A exceeds 50 weight % is a kind and an A-B-A (C-2) mold block copolymer ([ A / A and ]) at least. [ of an alkenyl aromatic compound ] [ polymerization-] B is the hydrogenation object of a polymerization block of a diene system hydrocarbon compound, and the content of A in total the combination at least with a kind of 50 or less weight % of resin 10 - 20 weight section, (D) It is the resin composition object which consists of the ethylene system (\*\*) polymer-aromatic vinyl graft polymer 1 - 20 weight sections with high graft efficiency.

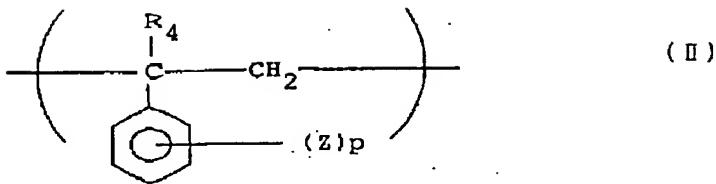
[0006] (A) polyphenylene ether resin (it abbreviates to PPE suitably below) used for this invention is a general formula. [Formula 1]



(-- the low-grade alkyl group of a carbon number 1-3, R2, and R3 are the low-grade alkyl groups of a hydrogen atom or a carbon number 1-3 R1 among a formula.) -- [ the structural unit expressed / it is the polymer which it has in a principal chain, and ] May be a homopolymer, or may be a copolymer and For example, the Pori (2, 6-dimethyl 1, 4 phenylene) ether, the Pori (2, 6-diethyl 1, 4-phenylene) ether, the Pori (2, 6-dipropyl 1, 4 phenylene) ether, the Pori (2-methyl, 6-propyl 1, 4 phenylene) ether, etc. should raise, and be -- [ \*\* ] A Pori (2, 6-dimethyl 1, 4 phenylene) ether, 2, 6-dimethylphenol and 2, 3, and 6-trimethyl phenol copolymer is desirable in particular.

[0007] The polymer of (B) alkenyl aromatic compound used for this invention is resin which includes the structural unit shown by the following general formula at least 25weight % or more in the polymer.

[Formula 2]



(A hydrogen atom or a low-grade alkyl group, and Z show a halogen atom or a low-grade alkyl group R1 among a formula, and p is the integer of 0 or 1-3.)

As a concrete example, polystyrene, high impact polystyrene, a styrene butadiene copolymer, A styrene butadiene AKURIRUNITORIRU copolymer, a styrene alpha-methylstyrene copolymer, A styrene maleic-anhydride copolymer, a styrene methylmethacrylate copolymer, an ethylene styrene copolymer, ethylene propylene butadiene SUCHIRENKOPORIMA, etc. are mentioned. Among these, especially high impact polystyrene is desirable and the rubber denaturalized of rubber components, such as polybutadiene, Butadiene Styrene rubber, or EPDM, is contained in this high impact polystyrene.

[0008] [ block copolymer / which is used for this invention / (C) A-B-A mold ] It is the triblock copolymer which consists of the polymerization block A of an alkenyl aromatic compound, and the polymerization block B of a conjugated diene hydrocarbon compound, or its hydrogenation object, and at least two or more sorts from which the content of A differed mutually are added. Namely, the A-B-A mold block copolymer with which the content of A (C-1) component exceeds 50 weight %, desirable -- the content of at least one sort from 60 to 80weight % of an A-B-A mold block copolymer, and A (C-2) component -- less than 50weight % of an A-B-A mold block copolymer -- at least one sort is preferably chosen from 20 to 40weight % of an A-B-A mold block copolymer. Although the molecular weight in particular of these A-B-A mold block copolymers is not limited, as for the thing of 100,000-300,000, 70,000-200,000 is [ former ] desirable about the latter on physical-properties balance. As these concrete examples, the hydrogenation object (it outlines Following SEBS) of styrene Butadiene Styrene and the hydrogenation object (it outlines Following SEPS) of a styrene isoprene styrene copolymer are raised. As (C-1), it is marketed in trade names, such as Clayton G1651 and SEPUPTON 4055, as SEPUPTON 2104 and (C-2).

[0009] [ graft polymer / which is used for this invention / with high (D) graft efficiency / ethylene system (\*\*\*) polymer-aromatic vinyl ] It is the resin composition object to which the ethylene system (\*\*) polymer was made to carry out the graft of the aromatic vinyl compound, for example, is obtained by kneading a graft precursor with an addition polymer under an elevated temperature. Water is made to suspend the ethylene system (\*\*) polymer 100 weight section with said graft precursor. Apart from this, a kind of radical (\*\*) polymerization nature organic peroxide, or two sorts or more of mixture to said aromatic vinyl monomer 100 weight section in the aromatic vinyl monomer 5 - the 400 weight sections 0.1 - 10 weight section, And the solution in which 0.01 - 5 weight section was made to dissolve a radical initiator to the total amount 100 weight section of an aromatic vinyl monomer and radical (\*\*) polymerization nature organic peroxide is added. It heats at 60-65 degrees C preferably on the conditions from which disassembly of a radical initiator does not arise substantially. An aromatic vinyl monomer, radical (\*\*) polymerization nature organic peroxide, and a radical initiator are made to sink into an ethylene system (\*\*) polymer. When it sinks into the amount used to a vinyl monomer, radical (\*\*) polymerization nature organic peroxide, and a radical initiator 50% or more, respectively, It is the resin composition object which the temperature of this aqueous suspension is made to rise, carries out the graft copolymerization of an aromatic vinyl monomer and the radical (\*\*) polymerization nature organic peroxide into an ethylene system (\*\*) polymer at 80-85 degrees C preferably, and is obtained.

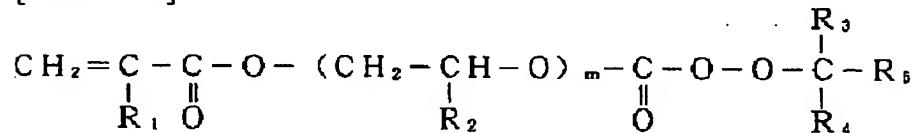
[0010] Fusion kneading of the obtained graft precursor is carried out with an addition

polymer. An ethylene system (\*\*) polymer-aromatic vinyl graft polymer with high graft efficiency is obtained by the above operation. Here, an ethylene system (\*\*) polymer is a copolymer of the homopolymer of ethylene or ethylene, and olefins, such as a propylene. A lower density ethylene polymer is mentioned as a desirable example of an ethylene system (\*\*) polymer. the consistency of this lower density ethylene polymer -- 0.910-0.935g/cm<sup>3</sup> that -- although -- it is desirable and, specifically, a copolymer with the ethylene homopolymer and ethylene which are obtained by a high-pressure-polymerization method, and the alpha olefin for consistency adjustment, for example, a propylene, butene-1, and a pentene 1 is raised.

[0011] Even when the pellet type with a particle size of 1-5mm of the configuration of this lower density ethylene polymer is also powdered, it is good. As for these, it is desirable to use properly by the blending ratio of coal of the lower density ethylene polymer in a graft-ized precursor. For example, a powdered thing is desirable, when the lower density ethylene polymer in a graft-ized precursor is 50 weight % or more and it is a pellet type and less than 50 weight %. The polymer of an aromatic vinyl compound is a polymer of the styrene permuted by styrene, the halogen atom, or the low-grade alkyl group. Specifically, polymers, such as styrene, methyl styrene, ethyl styrene, dimethyl styrene, isopropyl styrene, chloro styrene, alpha-methylstyrene, and alpha-ethyl styrene, can be mentioned. 10,000-200,000 is suitable for the weight average molecular weight of this polymer.

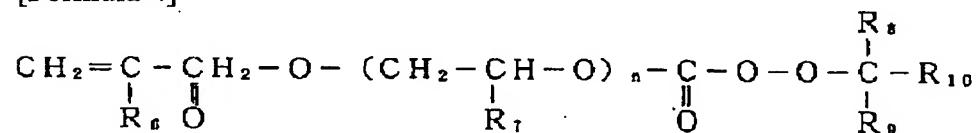
[0012] Moreover, radical (\*\*) polymerization nature organic peroxide is a compound expressed with next \*\* 3 or next \*\* 4. Specifically, t-butylperoxy AKURIROIROKISHI ethyl carbonate and t-butylperoxy allyl carbonate can be illustrated as a desirable thing.

[Formula 3]



(R1 shows the alkyl group of a hydrogen atom or a carbon number 1-2 among a formula, a hydrogen atom or a methyl group, and R3 and R4 show the alkyl group of a carbon number 1-4 R2, and R5 shows the alkyl group of a carbon number 1-12, a phenyl group, an alkylation phenyl group, or the cycloalkyl radical of a carbon number 3-12 respectively.) m is 0, 1, or 2.

[Formula 4]



(R6 shows the alkyl group of a hydrogen atom or a carbon number 1-4 among a formula, a hydrogen atom or a methyl group, and R8 and R9 show the alkyl group of a carbon number 1-4 R7, and R10 shows the alkyl group of a carbon number 1-12, a phenyl group, an alkylation phenyl group, or the cycloalkyl radical of a carbon number 3-12 respectively.) n is 0, 1, or 2. Moreover, as a radical initiator, well-known radical initiators, such as benzoyl peroxide, are used.

[0013] When the obtained graft precursor carries out fusion kneading with an addition polymer, an ethylene system (\*\*) polymer-aromatic vinyl graft polymer with high graft efficiency is obtained. Here, an addition polymer is a polymer which consists of either or the both sides of a polymer of the styrene permuted by the copolymer, styrene, halogen atom, or low-grade alkyl group of the homopolymer of ethylene or ethylene, and olefins, such as a propylene. 20,000-200,000 is suitable for the weight average molecular weight of an addition polymer.

[0014] Although the ratio in particular of the ethylene system (\*\*) polymer used about the

graft polymer of this invention and an addition polymer is not limited, 15 to 85 weight % has the desirable rate of an ethylene system (\*\*\*) polymer to both total amount, and its 25 to 70 weight % is more desirable. When compatibility is taken into consideration, 30 to 50 weight % is the most desirable. Graft efficiency of the description is [ graft polymer used by this invention ] high. It is graft efficiency (The graft-ized aromatic vinyl monomer) / (used aromatic vinyl monomer) x 100 If expressed, the graft efficiency of the graft polymer of this invention will reach to 50 to 60%, and will far exceed the graft efficiency (about 10%) of the usual graft polymer. As a desirable ethylene system (\*\*) polymer-aromatic vinyl graft polymer, what is marketed by the trade name of MODIPA is mentioned.

[0015] The resin composition object of the invention in this application can be manufactured by the facility and method which are generally used for manufacture of a thermoplastics constituent. For example, it is possible to mix the component which constitutes a resin composition object with mixers, such as a tumbler, to knead and carry out extrusion molding using the extruder of one shaft or two shafts, and to manufacture as a pellet type etc.

[0016] You may add inorganic bulking agent material, such as flame retarders, such as a halogen system and a \*\*\*\*\* system, various kinds of pigments, an ultraviolet ray absorbent or a glass fiber, and a carbon fiber, to the resin composition object of this invention.

[0017]

[Example] Although explained still more concretely with an example, this invention is not restricted to this. The physical-properties check of the PPE system resin composition object of this invention was performed by the following method.

The shaping method; a table 1, 2 The shown PPE resin composition object of the blending ratio of coal was mixed for 10 minutes with the tumbler mold blender, and it pelletized by performing fusion kneading with the barrel preset temperature of 270-290 degrees C with the Toshiba nature twin screw extruder TEM35 mold. This pellet was fabricated at 90 degrees C with the making machine of 50t of clamping pressure after 5-hour desiccation, and the test piece for physical-properties measurement was fabricated with the molding temperature of 290 degrees C.

Physical-properties measuring method (a table 3 and the physical properties shown in 4 were based on the following measuring methods.)

Izod impact resistance value: ASTM According to D-256, it measured at thickness 1/8", the temperature with a notch of 23 degrees C, and -30 degrees C. (Kg/cm<sup>2</sup>)

DTUL:ASTM According to D-648, it measured by two in thickness 1/4", and a 18.6kg/cm load. (degree C)

floating length: -- the Japan Steel Works Co., Ltd. -- Make With the J100SA-2 die-forming machine, bar flow length (mm) 290 degrees C of cylinder temperatures, the injection pressure of 1000kg/cm<sup>2</sup>, 2mm in thickness, and 20mm in width was measured.

Appearance: With the test piece which measured the above-mentioned floating length, the layer exfoliation situation of the gate was observed and it ranked as follows.

O : -- layer-exfoliation-less \*\*:layer exfoliation intensity slight x:layer exfoliation intensity -- remarkable [0018] The example 1PPE(limiting viscosity 0.45 in inside of Mitsubishi Gas Chemical Co., Inc. make and 25-degree-C chloroform) 40 weight section, The high-impact-polystyrene resin (product [ made from Mitsubishi Kasei Pori Tech ], trade name diamond REXX HT 478) 49 weight section, The hydrogenation SEPS-A(Kuraray Co., Ltd. make, trade name SEPOTON 2104) 5 weight section, The hydrogenation SEPS-B(Kuraray Co., Ltd. make, trade name SEPOTON 4055) 3 weight section, The LDPE-g-PS(MODIPA A-1101 by Nippon Oil & Fats Co., Ltd.) 3 weight section, the stabilizer-1 (Sumitomo Chemical Co., Ltd. make, Sumi Reiser BHT) 0.2 weight section, and the stabilizer-2 (product [ made from SANDOZ ], San Dos \*\*-\*\* P-EPQ) 0.2 weight section It blended and the test sample was produced on the above-mentioned conditions.

[0019] It was presupposed in the example 2 example 1 that it is the same as that of an

example 1 as high-impact-polystyrene resin except having blended GPPS made from the Mitsubishi Kasei Pori tech, and the mixed elegance of 1:1 with trade name diamond REXX HF 77 with HT478.

[0020] The mixing ratio of the polystyrene resin used in the example 3 example 2 was set to 2:1. It was presupposed except this that it is the same as that of an example 1.

[0021] The example 4PPE(what was used in example 1) 35 weight section, the impact resistance polystyrene resin (what was used in example 1) 40 weight section, hydrogenation SEPS-A, 7 weight sections, hydrogenation SEPS-B, 8 weight sections, LDPE-g-PS, 10 weight sections, and others presupposed that it is the same as that of an example 1.

[0022] Instead of MODEIPA, 3 weight sections combination of the EPR (Product made from EXXON, trade name screw TARON 878P) was carried out in the comparative example 1 example 1. Others presupposed that it is the same as that of an example 1.

[0023] A stabilizer 1 and 2 were blended with the comparative example 2PPE(what was used in example 1) 40 weight section, and the polystyrene resin (what was used in example 1) 60 weight section like the example 1.

[0024] The comparative example 3PPE(what was used in example 1) 40 weight section, the polystyrene resin (what was used in example 1) 55 weight section, hydrogenation SEBS (Product made from SHELL, trade name Clayton G1651, 5 weight sections, a stabilizer 1, and 2 were blended like the example 1.)

[0025] Eight weight sections combination of the polystyrene resin 52 weight section and the hydrogenation SEBS (product made from SHELL trade name Clayton G1651) was carried out by comparative example 4 comparative example 3. The above recipe was shown in a table 1 and 2, and the physical-properties evaluation result was shown in a table 3 and 4. It describes below about the notation showing each component in a table.

A-1) PPE resin (limiting viscosity in the inside of the Mitsubishi Gas Chemical Co., Inc. make and 25-degree-C chloroform 0.45)

B-1) HIPS (the product made from Mitsubishi Kasei Pori Tech, diamond REXX HT 478) What mixed B-2HT478 and GPPS (the product made from Mitsubishi Kasei Pori Tech, diamond REXX HF 77) by 1 to 1.

B-3) What mixed Above HIPS and GPPS by 2 to 1.

C-1) Hydrogenation SEPS (SEPUTON 2104)

C-2-1 hydrogenation SEPS (SEPUTON 4055)

C-2-2) Hydrogenation SEBS (Clayton G1651)

D-1) LDPE-g-PS (MODEIPA A1101)

E-1) EPR (bis-TARON 878P)

S-1) Sumi Reiser BHTS-2 sand SUTABU P-EPQ [0026]

[Table 1]

Table 1 \*\* Part example 1 example 2 example 3 example 4A-140404035B-1490040B-205000B-300500C-15557C-2-13 3 3 8 D-1 3 2 2 10 S-1 0.2 0.2 0.2 0.2 S-2 0.2 0.2 0.2 0.2  
[0027]

[Table 2]

Table 2 \*\* Part comparative example 1 comparative-example 2 comparative-example 3 comparative-example 4A-140404040B-149605552C-15000C-2-13000C-2-20058E-13 0 0 0 S-1 0.2 0.2 0.2 0.2 S-2 0.2 0.2 0.2 0.2 [0028]

[Table 3]

table 3 item Example 1 Example 2 Example 3 Example 4 Izod 35 17 24 50 (23 degrees C)  
Izod 12 7 10 20 (-30 degrees C)

Bar flow 210235220 170 DTUL 120 120 120 117 Appearance O O O \*\* [0029]

[Table 4]

table 4 item Comparative example 1 Comparative example 2 Comparative example 3 Comparative example 4 Izod 50 11 17 20 (23 degrees C)

Izod 20 6 8 10 (-30 degrees C)

Bar flow 160220185170 DTUL 118 119 120 120 Appearance x O O x [0030]

[Effect of the Invention] The resin composition object obtained by this invention is an ingredient for large-sized mold goods like [ it is good, and / it is the thing which has practically high value, which is moreover seen in the case of elastomer addition of immiscible nature and which also suppressed the layer exfoliation phenomenon, and ] the inner package panel material of an automobile with suitable fluidity and heat-resistant and shock-proof (low temperature) physical-properties balance.

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